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# Array of chromium doped nanostructured $TiO_2$ metal oxide gas sensors

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**Abstract**

The aim of this work was to design and test an array of sensors based on nanocrystalline of $TiO_2$:Cr (0.1–10 at.% Cr) for reliable and reproducible gas detection. Thermally modulated responses of metal oxide nanosensors to hydrogen, methane and propane (0 – 3000 ppm) at various humidity levels (up to 75%RH) were studied. The sensors operated upon sinusoidal temperature profile over a temperature range of 240 – 300°C. The dynamic responses upon target gas exposure were recorded, processed and analyzed. The change of the conductivity type from n-type to p-type was observed at 1 at.% Cr doping. The $TiO_2$:Cr (5 at.% Cr) nanosensor was found to exhibit the highest response to hydrogen.

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*Keywords:* gas sensors, Cr dopants, sensor array, temperature modulation

## 1. Introduction

Metal oxide gas sensors are commonly used for detection of reducing and oxidizing gases. However, significant drawbacks like cross-sensitivity to interfering gases and humidity limit the number of practical applications [1]. An improvement in sensing performance of nanooxide gas sensors was first presented by Yamazoe [2] in 1991. Since then, substantial efforts have been made in the research of nanostructured materials for gas sensing. Nevertheless, nanostructured metal oxides still lack the desired selectivity. Therefore, techniques like constructing sensor arrays and modulation of the sensor operating temperature have been investigated in order to enhance sensor performance [3, 4].

Many attempts have been undertaken in the past to exploit the influence of a trivalent Cr dopant acting as an acceptor type impurity on the electrical and gas sensing properties of $TiO_2$ [5 – 8]. It has been demonstrated that doping improves the response time and sensitivity [5, 6]. Moreover, it enables to decrease the baseline resistance of


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the sensor thus widens the signal detection range [5 - 8]. Furthermore, it has been observed that Cr additive can change the type of conductivity from n to p [47, 48].

The aim of this work is to investigate the sensing performance of the array of $TiO_2$:Cr nanosensors upon temperature modulation in order to decrease the average operating temperature and power consumption. It was presented in [9] that sensors obtained from $TiO_2$:Cr nanopowders showed promising characteristics in response to hydrogen when measured under constant temperature conditions. The responses were large and reproducible. The electrical resistance decreased upon hydrogen exposure up to 1 at.% Cr while the reversed effect was observed at 5 at.%. The sensor performance clearly improved with a decrease in the operating temperature. Contrary to the static measurements performed previously [9] this work covers the dynamic gas sensing properties of $TiO_2$:Cr nanosensors and the humidity influence.

## 2. Experimental details

An array consisting of seven different nanostructured metal oxide gas sensors has been designed and tested. The sensors are comprised of chromium doped $TiO_2$. Nanocrystalline powders of $TiO_2$:Cr (0.1–10 at.% Cr) obtained by flame spray synthesis (FSS) described in detail in [10, 11] were used as a base material for preparation of gas sensors. The analysis of structure and morphology of nanopowders obtained by flame spray synthesis (FSS) have been performed in [10, 11]. The mechanism of Cr incorporation into $TiO_2$ has been proposed in [10, 11]. Nanopowders were calcined at 400°C in a form of circular tables, the morphology of which is similar to that of starting materials. Characterization of nanopowders (Tab. 1) was carried out by thermogravimetry (TG), Brunauer–Emmett–Teller (BET) adsorption isotherms, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The detailed study of physical and sensing properties at a constant temperature can be found in [9].

Table 1. Basic physical properties of the studied Cr-doped $TiO_2$ nanopowders.

| at.% Cr | Specific surface area SSA from BET ($m^2/g$) | Grain size from BET (*nm*) | Crystallite size from XRD (*nm*) | |
|---|---|---|---|---|
| | | | Anatase | Rutile |
| 0 | 37.5 | 41.5 | 26.8 | 13.6 |
| 0.1 | 48.4 | 32.5 | 21.2 | 9.6 |
| 0.2 | 47.6 | 32.7 | 22.7 | 11.2 |
| 0.5 | 72.2 | 21.5 | 15.7 | 13.0 |
| 1 | 87.1 | 17.8 | 13.8 | 9.3 |
| 5 | 126.6 | 12.1 | 9.1 | 7.5 |
| 10 | 160.7 | 9.5 | 6.0 | 6.5 |

The constructed array of gas sensors operates at temperatures modulated from 240°C to 300°C as a sinusoidal function within a period of 8 min. Sensing properties are measured in a self-assembled experimental system described in detail in [4]. The measurements of the gas sensor responses have been carried out as functions of gas concentration and relative humidity level. The responses of the sensors have been recorded upon various hydrogen, methane and propane concentrations (0 – 3000 ppm) at humidity levels of 0-75%RH.

## 3. Results and discussion

The sinusoidal changes in the array operating temperature lead to periodic changes in the sensors electrical resistance. The resistance is measured every 1 sec. hence, the resistance **r** data vector over one temperature modulation period consists of N = 480 samples:

$$\mathbf{r} = \begin{bmatrix} r_1 & r_2 & \cdots & r_N \end{bmatrix} \tag{1}$$

The resistance variations in time over one temperature modulation period to various hydrogen concentrations are presented in Fig. 1. As one can observe the amplitude of the resistance change is dependent on the hydrogen concentration. Furthermore, two types of conduction are revealed (p and n-type). Results indicate that undoped $TiO_2$ and $TiO_2$ doped with up to 1 at.% Cr behave as n-type semiconductors, where starting from 1 at.% Cr the samples exhibit p-type conductivity.

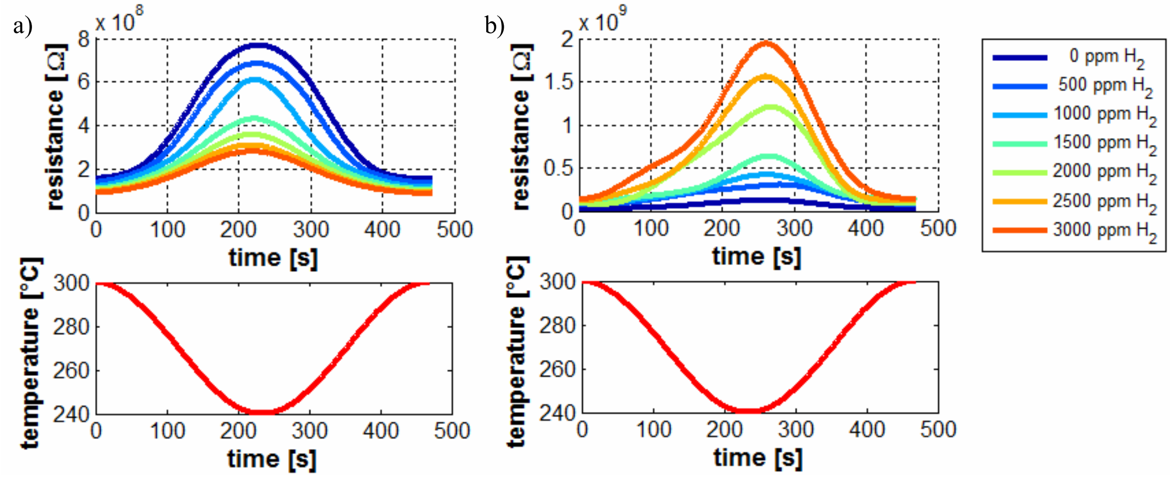


Fig. 1. Resistance changes of (a) $TiO_2$:Cr (0.1 at.% Cr); (b) $TiO_2$:Cr (5 at.% Cr) nanosensors upon one temperature modulation cycle (240 - 300°C) to different $H_2$ concentrations at 0%RH.

The dynamic response S of a sensor operating upon temperature modulation can be defined as:

$$S = \frac{R_A - R_{A0}}{R_{A0}} \tag{2}$$

were: $R_{A0}$ is the amplitude of the resistance change in a reference atmosphere (air) and $R_A$ is the resistance change amplitude change upon exposure to the target gas. Moreover, we define this amplitude change over one temperature modulation cycle as a difference between the maximum and minimum resistance **r** during this period. The responses of $TiO_2$:Cr (0.2 at.% Cr) and $TiO_2$:Cr (10 at.% Cr) nanosensors to hydrogen at various humidity levels are presented in Fig. 2.

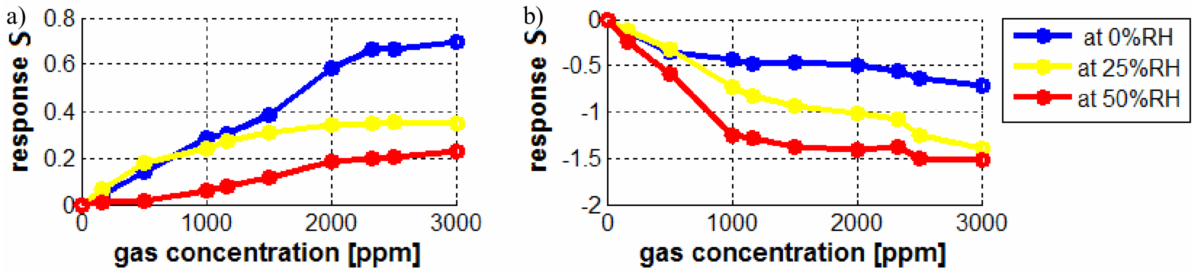


Fig. 2. Responses S of (a) $TiO_2$:Cr (0.2 at.% Cr); (b) $TiO_2$:Cr (10 at.% Cr) nanosensors upon temperature modulation (240 - 300°C) to different concentrations of hydrogen at various relative humidity levels.

As presented in Fig. 2 a significant humidity influence on the response can be observed. For the $TiO_2$:Cr (0.2 at.% Cr) nanosensor the response decreases while in the case of $TiO_2$:Cr (10 at.% Cr) the response increases with the increase in the relative humidity level. This is related to n to p transition at 1 at.% Cr. The absolute values of all responses of the sensors in the array to hydrogen and methane are presented in Fig. 3 in a form of radar plots.

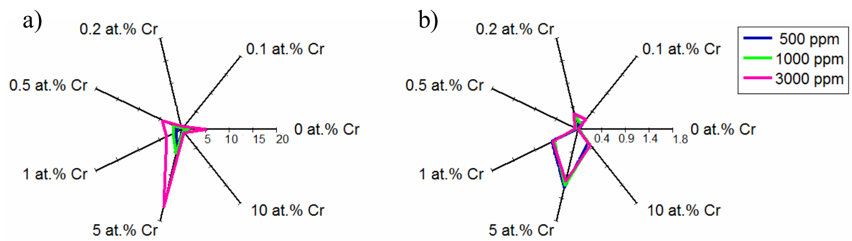


Fig. 3. Radar plots presenting the absolute values of the responses of all the nanosensors in the array to (a) hydrogen; (b) methane at 0%RH.

As one can observe in Fig. 3 from all of the sensors in the array the $TiO_2$:Cr (5 at.% Cr) exhibits the highest response to hydrogen. Moreover, some sensors like $TiO_2$:Cr (0.5 at.% and 0 at.% Cr) present almost no response to methane, while the response of other sensors to methane is small compared to the response to hydrogen.

## 4. Conclusions

The results obtained during our research allow us to draw the following conclusions. Each sensor in the array has different sensing properties what is the result of different Cr doping. Furthermore, a change of the conductivity type from n-type to p-type is observed at 1 at.% Cr doping. Similar to the results presented in [9] the $TiO_2$:Cr (5 at.% Cr) nanosensor exhibits the best hydrogen sensing properties. Significant response to hydrogen can be observed, compared to small response to methane and propane. Finally the adopted method of temperature modulation decreases the overall power consumption because the average operating temperate is lower as compared to sensors operating at a constant temperature.

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